

COMPOSITION OF NATURAL RECYCLE SOLVENT IN THE HYDROGENATION OF AUSTRALIAN COALS

by Norbert V. P. Kelvin and Mervyn J. Oliver

Australian Coal Industry Research Laboratories Ltd.
P.O. Box 83, North Ryde. New South Wales. 2113.

INTRODUCTION

ACIRL is engaged in an Australian Government supported program of research into the hydrogenation of Australian coals using known hydrogenation technology, principally that being developed in West Germany, as described, for example, by Romey et al¹. The conditions used by the West Germans would be considered severe with pressures around 30-40 MPa, temperatures up to 475°C for higher rank coals and added iron catalysts. Under these conditions the effect of solvent or vehicle composition on hydrogenation yields may be overshadowed by the high donor activity of dissolved hydrogen at high pressures and temperatures. However, operation at high pressures imposes cost penalties at both commercial and research scales. For this reason all our work to date has been done at more moderate severity, namely, 21 MPa and correspondingly reduced temperatures in the range 400-435°C to avoid excessive solvent vaporization in the preheater and reactor zones. Our moderate severity experiments have provided the base case distillate oil yield data for three main groups of important Australian coals considered suitable for hydrogenation ranging in rank from lignite (brown coal) to high volatile bituminous. Under moderate severity the effects of solvent composition and hydrogen partial pressure may be of about equal importance. Hence it was considered necessary to study the composition of recycle solvent during actual hydrogenation runs with Australian coals.

EXPERIMENTAL

The 1 kg/h slurry continuous reactor used in this study and hydrogenation data obtained have been reported in ACIRL reports²⁻⁵. In this study, successive samples of slurry oil (recycle solvent) were taken over three continuous runs lasting a total of 440 hours. The coal was Queensland sub-bituminous (lignitic), process severity 21 MPa, 430°C preheater, 415°C reactor, first four passes run without added catalyst then subsequent passes with added red mud 3-5% on coal and sulfur 1% on coal followed by a proprietary improved red mud, hydrogen/coal feed ratio 18/100 and solvent/coal ratio 2/1. The reactor was a 3-compartment partial backmix reactor. Slurry residence time in the reactor was estimated at about 2-3 hours but this could not be ascertained with certainty in these runs. The analysis of the coal used in these runs is given in Table 1.

Recycle solvent was recovered by atmospheric plus vacuum distillation of 3-4 kg batches of product slurry in laboratory glassware and used to make up fresh slurry with coal and added catalyst. Part of the recycle solvent was taken as product.

Samples of successive solvent batches (i.e., at every distillation of 3-4 kg product slurry) were analysed by infra red spectroscopy, GC-MS, titrimetry, etc. The GC-MS (DuPont DP-1) used a 47 m SCOT column (OV-101 on Chromosorb W) and a temperature program of 35-270°C at 2.61 K/min. Mass percentages of the significant components identified were estimated from flame ionization

detector responses. Portions of the solvent samples were also titrated for total phenolics and nitrogen bases. Fuller details of this part of our overall studies are given by Oliver⁶.

RESULTS AND DISCUSSION

Figure 1 shows the catalyst addition schedule and corresponding distillate yields together with the variation in solvent aromatic hydrogen content. Note that the catalyst used in the last 5-6 passes was a proprietary improved presulfided red mud. The effects of red mud and changing red mud on distillate yield are very clear. Red mud increased the degree of hydrogenation of coal-derived material as shown in Figures 1 and 2. The relative aromatic hydrogen content (Figure 1). Figure 1 shows that the relative aromatic hydrogen content (estimated from infra-red spectra) which remained stable from the 2nd to the 4th pass and then abruptly decreased after the 4th pass. This indicates that more hydrogen is taken up by the solvent and the coal-derived oils when catalyst is added.

The particular coal used in the solvent composition study contained a high proportion of exinite which produced noticeable quantities of waxes and paraffins. All unsaturates were expected to be hydrogenated to saturates at our conditions and this was confirmed by chemical analysis. Paraffins gradually accumulated with successive passes of solvent as shown in Figure 2.

The rate of increase in paraffins content rose from 0.6% per pass to 1.2% per pass just after the 4th pass when catalyst was added.

The paraffin content of equilibrated recycle solvent used with this particular coal appeared to line out at around 20-25%. As we always made more solvent than was required to maintain solvent balance, part of the solvent could be regarded as product. Accordingly, the build up of paraffins could indicate that this particular coal may be a suitable feedstock for diesel fuel production. The distribution of paraffins by length of carbon chain length in lined-out recycle solvent is given in Table 2.

Phenolics and nitrogen bases in the recycle solvent also stabilised after 4-5 passes as shown in Figure 2. From these data, it appears that the addition of catalyst has little if any effect on the accumulation of either phenolics or nitrogen bases probably indicating that the formation of both these classes of compounds is independent of catalyst.

Figures 1 and 2 also show that the recycle solvent equilibrated at about 10-15 passes, although some groups of compounds were observed to stabilise in 2-4 passes.

Hydrogen balance data from this series of runs and elemental analyses of the solvent samples indicated that the hydrogen uptake declined from about 1% wt of the solvent per pass to negligible uptake at equilibrium.

The analysis of the equilibrated solvent by compound groups was 30% aromatics, 21% hydroaromatics, 19% phenolics, 23% paraffins and 7% other components. From these data alone the hydrogen donor power of the solvent cannot be determined. Further work with recycle solvents at different hydrogen partial pressures on Australian coals is planned to be done in batch autoclaves and mini autoclaves.

CONCLUSIONS

1. Iron-based catalysts are necessary to ensure high yields of hydrogenation distillate liquids from Australian coals.
2. Iron-based catalysts increase the proportion of saturated compounds in both product oils and recycle solvent but do not significantly affect the formation or disappearance of phenols and nitrogen-bases.
3. Natural recycle solvent equilibrates substantially within about 2-4 passes and almost definitely within 10-15 passes.

ACKNOWLEDGEMENTS

Support for this Project was provided under the National Energy Research Development and Demonstration Program administered by the Commonwealth Department of National Development and Energy. CSR Ltd., also provided funding for part of this work and prepared the improved red mud catalyst. Grateful acknowledgement is also made for the work of ACIRL staff involved in the project.

REFERENCES

1. ROMNEY, I., FRIEDRICH, F., and STROBEL, B., ACS Div. Fuel Chem. PREPRINTS, 26 (1), 76-83 (1981).
2. KELVIN, N.V.P., Oil and Chemicals from Coal-Construction and Commissioning of 1 kg/h Continuous Reactor Unit. Report P.R.78-2, ACIRL Ltd., Sydney, Feb. 1978.
3. KELVIN, N.V.P. and BENNETT, P., Hydroliquefaction of Australian Coals - Continuous Reactor Studies. Report P.R.79-10, ACIRL Ltd., Sydney, Oct.1979.
4. STAKER, R., LIM, B., and FREDRICKSON, P., Hydroliquefaction of Australian Coals - Continuous Reactor Studies on a Victorian Brown Coal, Report P.R.80-5, ACIRL Ltd., Sydney, June 1980.
5. STAKER, R., Hydroliquefaction of Australian Coals - Continuous Reactor Studies on Bituminous Coals. Report P.R.81-5, ACIRL Ltd., Sydney, August 1981.
6. OLIVER, M.J. Changes in Product Oil Composition during Continuous Hydroliquefaction of an Australian Black Coal. Report P.R.81-4, ACIRL Ltd., Sydney, May, 1981.

TABLE 1

ANALYSIS OF COAL USED IN RECYCLE SOLVENT EQUILIBRATION STUDY

PROXIMATE ANALYSIS

(% as analysed)

Moisture	7.6
Ash 8.3	
Volatile Matter	42.7
Fixed Carbon	41.4

ULTIMATE ANALYSIS

(% daf)

Carbon	77.8
Hydrogen	5.9
Nitrogen	1.0
Sulphur	0.4
Oxygen + errors	14.9

PETROGRAPHIC ANALYSIS

(% Volume)

Vitrinite	68
Exinite	21
Inertinite	7
Mineral Matter	4
Vitrinite Reflectance (R_o max) %	0.38

TABLE 2

PARAFFIN DISTRIBUTION IN LINED-OUT RECYCLE SOLVENT

<u>Carbon Chain Length</u>	<u>Approximate Percentage of Total Paraffins</u>
0 - 10	1
10 - 12	4
13 - 16	22
17 - 20	25
21 - 25	30
26 - 29	18
30 +	< 0.3

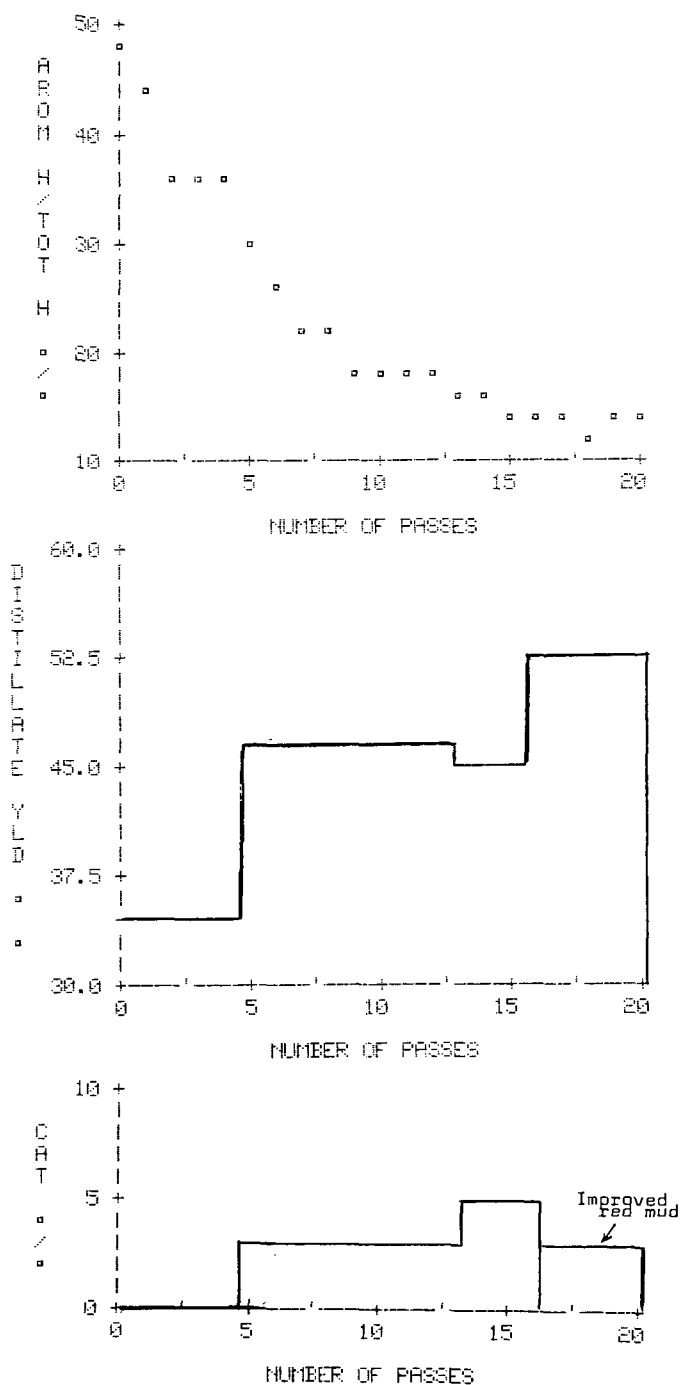


FIGURE 1. Effect of red mud on distillate yield and solvent aromaticity

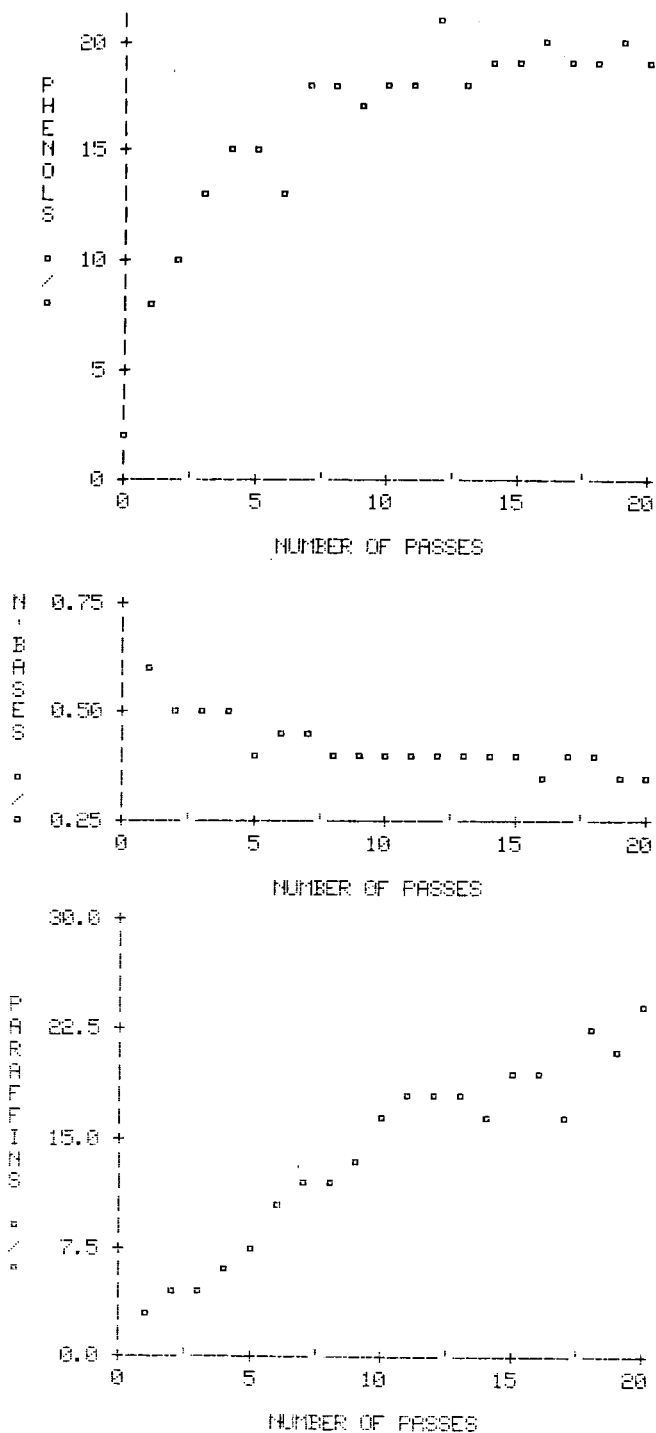


FIGURE 2. Recycle solvent characteristics